

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Coating Composition and Photographic Element Containing the Composition

We, GAF CORPORATION, (formerly General Aniline & Film Corporation,) a corporation organized and existing under the laws of the State of Delaware, United States of America, having its main office at 140 West 51st Street, City, County and State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coating compositions comprising a water-permeable colloid and more particularly, to gelatin coating compositions advantageously adapted for use in connection with high-speed coating methods.

As is commonly recognized in the coatings industry, it is highly desirable, if not essential, that water-permeable colloid, e.g., gelatin-containing coating compositions can be capable of application at relatively high coating speeds, and that the layers so deposited be of uniform and selected physical characteristics. The foregoing requirements are of primary import in operations associated with the preparation of photographic film elements. Ideally, coating aids contemplated for use in water-permeable colloid-containing compositions and especially those containing gelatin should:

- (1) Be of uniform quality and have uniform properties from batch to batch;
- (2) Enable the use of high-speed coating operations both in wet-On-wet and wet-on-dry coatings;
- (3) Be devoid of any tendency to impart streakiness or repellency to the water-permeable colloid;
- (4) Exhibit minimal sludge and/or foam formation;
- (5) Produce coatings having little or no tendency to slip;
- (6) Be non-photoactive

Heretofore, considerable difficulty has been encountered in connection with attempts to provide water-permeable colloid layers of the desired characteristics while utilizing coating speeds which are consonant with feasible commercial operation and satisfactory product throughput. With gelatin compositions for example, and to which no auxiliary coating aid has been added, there are invariably obtained coated layers which exhibit manifold defects including, e.g., the presence of numerous crescent-shaped uncoated areas, also referred to as repellency spots, such defects approximating the size of a pinhead with streaks or other such irregularities emanating from the

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points of the crescent and proceeding in a direction opposite to that of the coating. It is not unusual to find that lightly coated areas of 5—10 mm. in diameter will result.

In an effort to overcome or otherwise mitigate the foregoing and related disadvantages, the art has resorted to the use of a variety of coating aids. Saponin for example, despite its relatively wide-spread use as a coating aid in gelatin compositions of various types has nevertheless proved somewhat unsatisfactory. Although yielding a relatively uniform and even coating, this material being of natural origin, may often vary markedly from batch to batch in quality, composition and purity to the extent that one or more of the properties required in the photographic emulsion may be deleteriously affected.

As a consequence, considerable attention has been focused on the use of synthetic coating aids selected from a wide variety of surfactant materials of the anionic, cationic amphoterics and/or non-ionic types; including for example, the taurides, betaines and imidazolinium salts. Since materials of the latter type may be subjected to relatively precise conditions of manufacture, problems associated with variations in quality, composition and purity are substantially eliminated. Despite the foregoing advantage, however, the synthetic coating aids heretofore provided have nevertheless proved unsatisfactory in a number of important respects. As examples of the more important difficulties repeatedly encountered with the use of the latter materials and especially in connection with the preparation of photographic layers containing gelatin, there may be mentioned their tendency to produce streakiness and repellency spots that cannot be readily rewet with the consequent condition that the product tends to form "air-bells" on the emulsion surface during photographic processing. Such areas will often manifest themselves in the form of relatively small, undeveloped areas in the processed product due to the fact that in such areas the developer is incapable of penetrating into the emulsion layer. These defects are not only unsightly to the extent that retouching of the negative is often required, but more importantly, can be dangerously misleading when present on certain types of films particularly medical or industrial X-ray films.

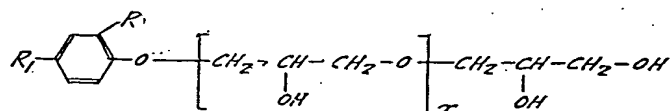
The foregoing and related problems become increasingly manifest in connection with "wet-on-wet" coating methods wherein the water-permeable colloid composition is applied to a wet substrate. The latter is, of course, a matter of prime commercial importance and especially in connection with plural coating operations wherein it is of utmost importance to eliminate any necessity for drying and thus the time which would otherwise be consumed thereby.

However, with the use of the coating aids heretofore provided, the "one pass-wet-on-wet" technique is found to be substantially inapplicable and accordingly, it becomes necessary to dry an applied layer prior to the application of an additional overcoating layer.

The present invention provides improved gelatin coating compositions advantageously adapted for application to both wet and dry surfaces *via* the use of high speed coating techniques in the virtual absence of skipping.

The coating aids used with the photosensitive gelatin emulsion compositions of the invention facilitate the attainment of coatings which are uniform and repellency-free without deleteriously affecting the emulsion.

The present invention provides improved water-permeable colloid coating compositions and coated elements prepared therewith and wherein such compositions contain as an essential ingredient a coating aid comprising a non-ionic surface active compound of the following general formula:



wherein R represents hydrogen or alkyl having from 1 to 18 carbon atoms inclusive, the said alkyl group being either straight chain or branched; R<sub>1</sub> represents alkyl containing from 8 to 18 carbon atoms inclusive which, again, may be either straight chain or branched and x represents a positive integer of from 3 to 30 inclusive, and preferably from 4 to 20.

Although specific reference will be made to gelatin throughout the present description, the term water-permeable colloid as used herein is to be understood as

encompassing water-soluble and/or dispersible materials whose aqueous solutions yield water-permeable films on drying. As particular examples of substances contemplated by the aforesaid definition, there may be mentioned the water-soluble cellulose esters of lactic or glycolic acid, partially hydrolyzed polyvinyl acetate, modified polyvinyl alcohols and water-soluble polyvinyl acetals. The colloid material may be suitably provided in the form of an aqueous dispersion, emulsion or suspension, such as would be the case with polymers derived from the polymerization of one or more acrylate monomers, e.g., ethylacrylate and methylmethacrylate. Such polymeric substances are customarily provided in latex form by the use of suitable emulsifying agents or suspending agents.

The truly surprising results provided by the compounds encompassed by the above formula when incorporated into water-permeable colloid-containing coating compositions in general and those comprising gelatin in particular, are made readily manifest by reference to the fact that such compounds permit the effective use of coating speeds which are at least double those necessarily employed heretofore with the virtual absence of the deleterious effects previously encountered, e.g., skipping. The coating of chilled photographic emulsions with surface gelatin layers employing surfactant materials currently provided for such purposes is invariably attended by severe problems of skipping such problems becoming more pronounced with the use of higher web coating speeds. It is self-evident, of course, that increased web speeds are vital for increased product throughput. As will thus be readily manifest, the advantages provided by the present invention when considered solely from an economic standpoint are of the first order of significance.

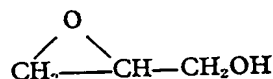
The coating aids of the present invention can be effectively employed in relatively small concentrations, i.e., of the order of 0.01% and lower by weight based upon the total weight of the coating composition. It will be understood, of course, that larger quantities may be employed to advantage, for example, in amounts ranging up to 2.5% to 3% based upon the total weight of coating composition. The particular proportions employed will depend to a large extent upon the ultimate use contemplated for the coating composition in question. Accordingly, the aforementioned concentrations are not particularly critical serving only to define those proportions found in general to yield optimum results. With specific reference to photographic utility, for example, in those instances wherein the gelatin is to be incorporated directly into a photographic silver halide emulsion, the higher concentration ranges will ordinarily be found to be most effective.

The photographic emulsions prepared utilizing the said glycidol polyether coating aids ordinarily comprise an aqueous solution of gelatin containing as the light-sensitive material a silver salt such as silver bromide, silver chloride, silver iodide as well as mixtures thereof. Such emulsions may be of the non-optically sensitized or optically sensitized type. When preparing the photographic emulsion, the glycidol polyether adduct may be added either before or after the addition of any of the other ingredients customarily employed in the manufacture of gelatin silver halide emulsions such as sensitizing dyes and hardeners. The particular coating procedure employed may comprise any of the standard methods promulgated in the industry for such purposes. For example, the substrate to be coated may be passed through a trough or other reservoir containing the coating composition. The coating may be applied to a greater thickness than that desired ultimately and thereafter subjected to the action of suitable levelling means such as a doctor-blade or an air-brush which causes run-back of the coating composition thereby resulting in the obtention of an even surface. In some instances, the coating method may involve a hopper technique in which the thickness of the layer is regulated by the rate at which the coating composition is deposited upon the base, the latter being transported in a direction adjacent thereto.

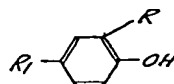
In addition, the glycidol polyether coating aids described herein may be employed to advantage in combination with one or more of the usual surface active materials employed in the coating of gelatin compositions. Such additional surfactant materials include, for example, the "IGEPONS" available commercially from the General Aniline Film Corporation with typical representatives including sodium, N-methyl-N-oleoyltaurate; sodium, N-methyl-N-caprylyltaurate and sodium-N-methyl-N-palmitoyltaurate, the imidazolinium class of surfactants such as any of those described in U.S. patent Specification 2,982,651 and the betaines, e.g., cetyl betaine. The aforesaid mixtures of surfactants are found to be particularly efficacious in connection with coating methods involving "wet-on-wet" applications.

The glycidol polyether non-ionic surfactants contemplated for use in accordance

with the present invention may be readily and conveniently prepared by heating glycidol which has the following structural formula:



with an alkyl phenol of the following general formula:



wherein R and R<sub>1</sub> have the aforescribed significance. Suitable alkyl phenols include the following representatives:

- p*-isononylphenol
- p*-isododecylphenol
- o*-, *p*-di-isononylphenol
- o*-, *p*-di-isododecylphenol
- p*-tert-octylphenol
- o*-*p*-di-tert-octylphenol
- p*-tert-octyl-*o*-isononylphenol
- p*-tert-octyl-*o*-isododecylphenol
- p*-sec-octylphenol
- p*-sec-dodecylphenol
- p*-sec-hexadecylphenol
- p*-sec-octadecylphenol
- o*-*p*-di-dodecylphenol
- p*-cetylphenol
- p*-octadecyl-*o*-cresol
- p*-tert-octyl-*o*-tert-butylphenol
- p*-iso-nonyl-*o*-tert-butylphenol,

and mixtures comprising 2 or more of the foregoing.

The reaction of the alkyl phenol and glycidol is preferably effected in the presence of an alkaline-reacting catalyst. Suitable catalysts for such purposes include the alkali metals, their oxides, hydroxides, alcoholates, phenates and cresolates, as well as mixtures comprising two or more of such materials. Typical examples of the aforescribed materials include sodium, lithium, potassium, sodium hydroxide, potassium hydroxide, sodium methanolate, lithium methanolate, sodium isopropylate, sodium octadecylate, sodium phenate, potassium phenate and sodium cresolate. The catalyst substance is most effectively employed in concentrations ranging from 0.1 to 2% by weight of the reaction mixture. The reaction may be carried out at elevated temperatures ranging from 100 to 200°C and preferably from 130 to 160°C. The temperature selected in a particular circumstance will quite naturally be influenced somewhat by the reaction rate desired as well as the properties and relative proportions of the reactants.

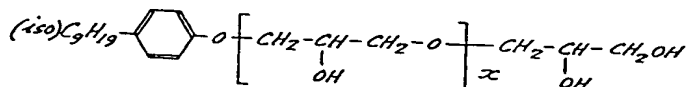
Since glycidol tends to react with itself and especially under the conditions recommended herein for preparing the glycidol-polyether derivative, it is advisable to add the glycidol to a previously prepared solution containing the desired quantities of alkyl phenol and catalyst. The glycidol addition should be controlled in such manner that the concentration of glycidol in the reaction medium is not allowed to exceed approximately 2% by weight based upon the total weight of the reaction medium. Particularly beneficial results are obtained when the glycidol concentration is maintained at a value approximating 0.5% by weight of the reaction medium.

The technique involved in the preparation of particular glycidol polyether derivatives found to be suitable for use in accordance with the present invention is described in detail in Belgian patent Specification 652,862. The following procedures are typical of the methods described therein.

#### A. Preparation of Glycidol/*iso*-nonylphenol Adduct

To a glass container provided with a rapid-speed agitator and reflux condenser is added a mixture comprising 220 gms. of technical grade *p*-isononylphenol (1 mole) and 1 gm. of potassium hydroxide. The mixture is subjected to agitation and heated

under a nitrogen atmosphere at a temperature of about 150°C. Approximately 432 gms. (6 moles) of glycidol are introduced into the alkyl phenol reaction mixture over a period of approximately 4-1/2 hours maintaining constant agitation. Incremental additions of potassium hydroxide are made at intervals throughout the course of the reaction in order to maintain a total potassium hydroxide concentration in the reaction mixture approximating its initial value. The terminal point in the reaction is indicated by a negative test for phenol. Upon completion of the reaction, water is added in an amount approximating to the total weight of the potassium hydroxide employed. The pH of the reaction media is brought to below 9 by the introduction of carbon dioxide and is thereafter allowed to cool to room temperature whereupon there is obtained a water-soluble, amber, viscous syrup which has the following general formula:



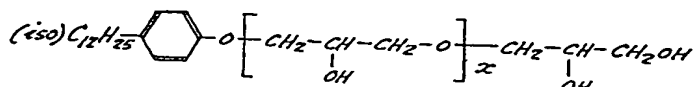
wherein x has an average value of 5. The *p*-isononylphenol employed in the above example is available commercially and can be readily prepared by the condensation of phenol with tripropylene in the presence of an acid catalyst.

#### B. Preparation of Glycidol/*p*-isododecylphenol Adduct

The procedure described in A is repeated utilizing the following proportions of reactants:

glycidol	173	gms.
<i>p</i> -isododecylphenol	88.5	gms.
potassium metal catalyst	0.24	gm.

The total quantity of glycidol is added to the alkyl phenol-catalyst mixture over a period of approximately 3 hours maintaining constant agitation. Upon completion of the reaction, there is obtained a water-soluble semi-solid and highly viscous compound which has the following general formula:



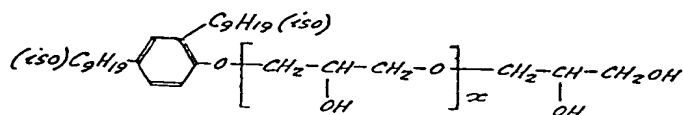
wherein x has an average value of 6.

#### C. Preparation of Glycidol/*o*-*p*-di-isononylphenol Adduct

The procedure described in A is repeated utilizing the following proportion of reactants:

glycidol	18.4	moles
<i>o</i> , <i>p</i> -di-isononylphenol	1	mole
potassium metal	1	gm.

The glycidol is added to the alkyl phenol-catalyst mixture over a period of approximately 8-1/2 hours maintaining constant agitation. Upon completion of the reaction there is obtained a water-soluble, semi-solid, highly viscous product of the following general formula:



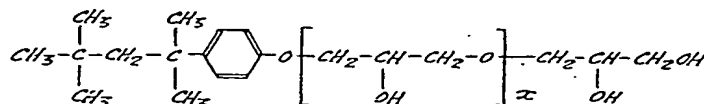
wherein x has an average value of 17.4.

#### D. Preparation of Glycidol/*p*-tert-octylphenol Adduct

The procedure described above is repeated utilizing the following proportions of reactants:

glycidol	5.5 moles
<i>p</i> -tert-octylphenol	1 mole
sodium metal catalyst	0.8 gm.

The glycidol is added to the alkyl phenol-catalyst mixture over a period of approximately 4 hours maintaining constant agitation throughout the addition. Upon completion of the reaction there is obtained a water-soluble, viscous syrup which analysis establishes to have the following structural formula:



wherein  $x$  has an average value of 4.5.

Products of the aforescribed type are readily available commercially and in this connection mention may be made of the surfactant materials bearing the trade name designations Non-Ionic Surfactant 3.5G, 6G and 10G available from the Olin Mathieson Chemical Corporation.

The uniquely beneficial and atypical properties imparted to gelatin coating compositions by the glycidol polyethers described herein will be made manifestly clear by the following examples.

#### EXAMPLE I

A coating composition is prepared comprising a gelatin silver halide photographic emulsion having a silver concentration of approximately 35 gms. per kg. of emulsion and a gelatin concentration of approximately 70 gms. per kg. of emulsion. Approximately 0.1% by weight of the total emulsion of the glycidol polyether described in A above is added. The emulsion is then coated onto a cellulose acetate film base via the air doctor blade technique at a web speed of approximately 112 ft. per minute. The coated sample is found to be totally free of defects such as typified by air bells. Moreover, the coated emulsion layer exhibiting excellent adhesion to the film base.

#### EXAMPLE II

Example I is repeated except that the silver halide emulsion layer is additionally provided with an overcoating layer comprising a 4% aqueous gelatin composition containing 0.4% by weight of sodium-N-decanoyl-N-methyltaurate, the latter composition being applied directly to the wet-chilled emulsion layer in the same coating pass and utilizing the same coating speed of 112 ft. per minute. The surface gelatin layer exhibited excellent adhesion to the subjacent silver halide emulsion layer and was found to be virtually devoid of coating defects. Moreover, despite the use of exceptional high coating speeds, no skipping tendency could be detected. In contradistinction, when the above procedure is repeated but utilizing a silver halide emulsion containing saponin in lieu of the glycidol polyether surface active agent, the skipping problem became intolerable at coating speeds in the neighbourhood of 40—45 ft. per minute.

#### EXAMPLE III

Example II is repeated except that the glycidol polyether adduct described in A is replaced by the same amount of that described in B. Similar results are obtained as regards the efficacy of coating speeds on the order of 110—115 ft. per minute.

#### EXAMPLE IV

Example II is repeated except that the glycidol polyether derivative employed is that described in C. Results similar to those described in the foregoing Examples are obtained.

## EXAMPLE V

Example II is repeated employing the glycidol polyether adduct described in D. Again, similar improvement was noted.

As previously indicated, the glycidol polyether surface active agents described herein may be utilized in combination with one or more of the more conventional surface active agents such as the imidazolinium compounds described in U.S. patent Specification 2,982,651, e.g.,

Monosodium salt of 2-undecyl-1-carboxymethyl-1-hydroxyethyl-imidazolinium hydroxide

Monosodium salt of 2-heptadecyl-1-carboxymethyl-1-hydroxyethyl-imidazolinium hydroxide

Disodium salt of 2-pentadecyl-1-carboxymethyl-1-hydroxyethyl-imidazolinium hydroxide

Monosodium salt of 2-nonyl-1-carboxymethyl-1-hydroxyethyl-imidazolinium hydroxide

Disodium salt of 2-heptadecenyl-1-carboxymethyl-1-hydroxyethyl-imidazolinium hydroxide

Disodium salt of 2-undecyl-1-carboxymethyl-1-( $\beta$ -carboxy-methyloxyethyl)-imidazolinium hydroxide.

It will further be understood that the nature of the additional surface active material is not a particularly critical factor in the practice of the present invention since any of the compounds conventionally employed in this regard may be used. For example, similar increases in coating speed are obtained with the use of, as additional surface active materials, protein condensation products of fatty acids, saponin, polyoxyethylene derivatives of long chain fatty acids and alcohols, sulphated oleic acid, dihexyl ester of sodium sulphosuccinate, sodium salt of an alkyl naphthalene sulphonic acid, sodium salt of tetrahydronaphthalene sulphonic acid, calcium glycerin phosphate, an alkylphenylpolyethylene glycol, oleic acid ester of hydroxyethane sulphonic acid, and sulphonates of high molecular weight aliphatic, aromatic and cycloaliphatic carboxylic acids.

Furthermore, the above described improvements are obtained whether the additional surface active material be of the non-ionic, anionic amphoteric and/or cationic variety.

The improvements provided by the present invention are also obtained with silver halide emulsions which contain colour formers which are provided with a solubilizing sulpho or carboxy group, and are therefore, soluble in alkali solutions, for instance, sodium hydroxide solutions. Such colour formers which upon colour development with a primary amino developer yield azomethine, quinoimine or azine dyes, are described in the literature.

The colour coupler may be of the non-diffusing type which, when added to the silver halide emulsion dispersed in a mixture of high boiling and low boiling solvents, forms packet-type emulsions with capsulated colour formers.

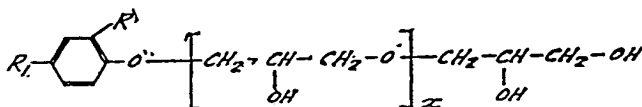
Although the present invention has been particularly described with reference to the preparation of photographic silver halide emulsions, it will be understood that the coating compositions provided by the present invention may comprise simply a mixture of gelatin or other water-permeable colloid with one or more of the glycidol polyether coating aids. Such compositions find utility in a wide variety of applications and may be applied as such to any number of substrate materials for purposes of providing a suitable overcoat. For example, they may be employed to advantage as protective coatings for paper, plastics such as films of cellulose nitrate, cellulose esters, e.g. cellulose acetate or cellulose acetate butyrate. In addition, they may be applied in the form of antihalation layers, antistatic layers, filter layers or in any type of gelatin layer which is coated from a composition consisting essentially of an aqueous solution of gelatin. For example, gelatin coating compositions intended for use as auxiliary layers or surface layers will usually contain the gelatin in amounts approximating 2-3% by weight of the total composition. However, when employed in the preparation of photographic emulsions, it is usually advisable to employ larger proportions of coating aid than would customarily be employed in aqueous solutions of gelatin intended for use as simple overcoatings. Moreover, in some instances, it may be advantageous to employ larger proportions even though the coating composition in question is intended for use as a simple auxiliary, i.e., non-image forming layer since, in general, larger concentrations are found to permit the more effective use of higher coating speeds. In general, increased proportions of coating aid are usually desirable

where the gelatin is employed in minor concentrations in the coating composition. The pH of the coating composition would ordinarily fall within a range of about 5 to 8. If applied as an auxiliary layer, e.g., as a non-curling layer in a photographic film element, an acid pH range is usually preferred.

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# WHAT WE CLAIM IS:—

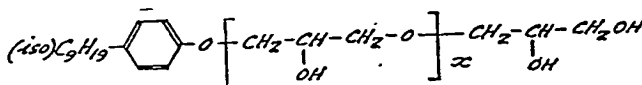
1. A coating composition comprising a water-permeable colloid and at least one compound of the following general formula:



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wherein R represents hydrogen or alkyl containing from 1 to 18 carbon atoms inclusive, R<sub>1</sub> represents alkyl containing from 8 to 18 carbon atoms inclusive and x represents a positive integer of from 3 to 30 inclusive.

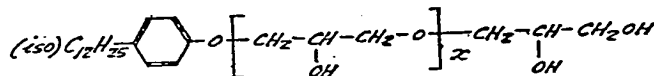
2. A composition according to claim 1, wherein the compound has the following general formula:



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wherein x has an average value of 5.

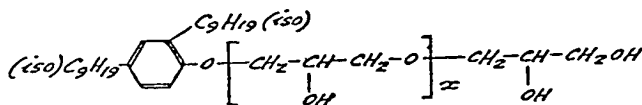
3. A composition according to claim 1, wherein the compound has the following general formula:



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wherein x has an average value of 6.

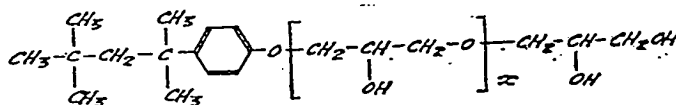
4. A composition according to claim 1, wherein the compound has the following general formula:



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wherein x has an average value of 17.4.

5. A composition according to claim 1, wherein the compound has the following general formula:



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wherein x has an average value of 4.5.

6. A composition according to any preceding claim, wherein the compound is present in an amount ranging from 0.01% to 3.0% by weight of the composition.

7. The coating composition claimed in any one of the preceding claims whenever in the form of a photographic silver halide emulsion.

8. A multi-layer, light-sensitive photographic element, wherein at least one layer comprises the composition claimed in any one of claims 1 to 7.



9. The coating composition claimed in any one of claims 1 to 7 substantially as herein described and exemplified.

10. The photographic element claimed in claim 8 substantially as herein described and exemplified.

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